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Preparation, properties and thermal decomposition of Y(III) and lanthanide(III) pyridine-2, 5-dicarboxylates

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Abstract

The conditions of the formation of Y(III) and lanthanide (III) (La–Lu) isocinchomeronates were studied, and their quantitative compositions and solubilities in water at 293 K were determined. The IR spectra of the hydrated complexes were recorded and their thermal decomposition in static air were determined. During heating the hydrated isocinchomeronates $Ln_2(C_7H_3NO_4)_3 \cdot nH_2O$ ($n = 6$–20) lose some (Ce, Pr, Dy–Tm) or all (Y, La, Nd–Tm, Dy, Lu) of their crystallization water molecules in one (Y, La, Pr–Dy, Er, Yb, Lu) or two (Ce, Ho, Tm) steps then the hydrated complexes decompose directly to the oxides (Y, Ce, Pr–Lu) or with intermediate formation of oxocarbonates $Ln_2O_2CO_3$ (La).

Keywords: DTA; DTG; Isocinchomeronic acid; IR; Lanthanon; TG

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1. Introduction

Pyridine-2,5-dicarboxylic acid $C_5H_3N(COOH)_2$, also known as isocinchomeronic acid, and other pyridinedicarboxylic acids and their derivates belong to interesting compounds with biological action and applications [1,2]. The ammonium, sodium and potassium isocinchomeronates are also soluble in hot water whereas the copper(II) and beryllium family ones are sparingly soluble [3,4]. A survey of literature shows that Cr(III) Co(II), Ni(II), Zn(II), Cu(II) [5,6]. Cd(II) [7] and Au(III) [8] complexes with isocinchomeronic acid have been studied. The complexes of rare earth elements (III) have not been prepared so far.

This work is a continuation of our study on physico-chemical properties of rare earth element pyridinedicarboxylates [9,10]. Its aim was to prepare of Y(III) and lanthanide

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(III) isocinchomeronates in the solid state and to examine their physico-chemical properties and thermal decomposition in air and the influence of the metal on the properties of the complexes in the lanthanide series. The properties and thermal decomposition of the complexes with various ligands change in the lanthanide series in different way.

The systematic study of the properties of the complexes of all series permit to establish some influence of the lanthanide on the properties of the complexes. Moreover new complexes can be interesting from biological point of view as other complexes with pyridinecarboxylic acids.

2. Experimental

2.1. Preparation

Complexes of Y(III) and lanthanides (III) from La to Lu (without Pm) with isocinchomeronic acid were prepared by adding stoichiometric quantities of a hot solution of ammonium isocinchomeronate (pH 5.0–5.5) to a hot solution of rare earth element chlorides (Ce(III) was used as its nitrate). The precipitates formed were heated in mother solution for 0.5 h at 343–353 K and then filtered off, washed with hot water to remove Cl^- and NH_4^+ ions and dried at 323 K to a constant mass.

2.2. Elemental analysis

The carbon, hydrogen and nitrogen contents were determined by elemental analysis using V_2O_5 as oxidizing agent. The metal contents were determined from TG curve and by ignition of the complexes to the oxides at 1253 K. The content of crystallization water was determined from TG curve and by heating the complexes isothermally at a suitable temperature. The obtained results are presented in Table 1.

2.3. IR spectra

The IR spectra of isocinchomeronic acid, and Y and separated lanthanide complexes and the sodium salt were recorded over the range 4000–400 cm^{-1} with an M-80 Carl Zeiss Jena spectrophotometer. The samples were prepared as KBr discs.

2.4. Thermal analysis measurements

The thermal stability of the prepared complexes was determined by using a Paulik-Paulik-Erdey Q-1500 D derivatograph. The TG, DTG and DTA curves were recorded. Measurements were made at a sensitivity of 100 mg (TG), 500 μV (DTG), 500 μV (DTA). Samples (100 mg) were heated in platine crucibles to 1273 K in static air at a heating of 10 K min^{-1}. The hydrated complexes were heated at a set temperature to a constant mass and the products were confirmed by their IR spectra and elemental analysis.

2.5. Determination of solubility

The solubility of the prepared complexes in water was determined at 293 K. The saturated solutions were prepared under isothermal conditions. The solubility was determined by the oxalate method. See Table 1.

3. Results and discussion

Isocinchomeronates of Y(III) and lanthanides from La to Lu (without Pm) were prepared as solid hydrates with the molar ratio of metal to organic ligand of 2:3 and general formula $Ln_2(C_7H_3O_4)_3 \cdot nH_2O$, where $n = 6$–20 (Table 1) having color characteristic of the lanthanide (III) ions. The degrees of hydration do not change regularly with increasing the atomic number in the lanthanide series.

The IR spectra of free isocinchomeronic acid, the prepared Y, lanthanide and sodium isocinchomeronates were recorded (Table 2). In the IR spectrum of free isocinchomeronic acid there is a single strong absorption band at 1729 cm^{-1} of COOH group. In the IR spectra of rare earth complexes this absorption band disappears and the bands of asymmetrical (ν_{as}) vibrations of the COO^- group appears at 1610–1640 cm^{-1} and 1580–1610 cm^{-1} and the bands of symmetrical (ν_s) vibrations at 1400–1420 cm^{-1} and 1370–1390 cm^{-1}, the absorption bands of ν(OH) appear with maxima at 3368–3480 cm^{-1}, the bands of valency vibrations of C–N in the pyridine ring appear at 1275–1390 cm^{-1} and 1100–1120 cm^{-1}, the bands of C–H appear with

Table 1
Analytical data and solubilities of yttrium and lanthanide isocinchomeronates in water at 293 K

Complex	% Ln		% C		% N		% H		Solubility 10^{-5}
	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	mol·dm^{-3}
Y_2L_3*$\cdot 8H_2O$	21.8	21.7	30.8	30.9	5.1	5.5	3.1	3.4	10
$La_2L_3 \cdot 14H_2O$	27.1	27.1	24.6	24.7	4.1	4.1	3.6	3.6	9.5
$Ce_2L_3 \cdot 16H_2O$	26.3	26.3	23.7	23.4	3.9	4.2	3.8	3.8	8.7
$Pr_2L_3 \cdot 14H_2O$	27.4	27.4	24.5	24.5	4.1	4.0	3.6	3.8	8.7
$Nd_2L_3 \cdot 7H_2O$	31.7	31.7	27.7	27.4	4.6	4.9	2.5	2.8	6.8
$Sm_2L_3 \cdot 7H_2O$	32.6	32.6	27.3	26.9	4.5	4.6	2.5	2.5	4.0
$Eu_2L_3 \cdot 6H_2O$	33.5	33.5	27.8	27.5	4.6	4.6	2.3	2.4	3.4
$Gd_2L_3 \cdot 12H_2O$	30.7	30.6	24.6	24.8	4.1	4.2	3.2	3.4	3.6
$Tb_2L_3 \cdot 6H_2O$	34.5	34.5	27.4	27.4	4.6	4.8	2.3	2.4	4.0
$Dy_2L_3 \cdot 12H_2O$	31.7	31.7	24.6	24.6	4.1	4.2	3.2	3.5	5.3
$Ho_2L_3 \cdot 14H_2O$	30.5	30.5	23.4	23.4	3.9	3.8	3.4	3.4	3.9
$Er_2L_3 \cdot 13H_2O$	31.5	31.5	23.7	24.0	3.9	4.2	3.3	3.3	5.2
$Tm_2L_3 \cdot 15H_2O$	30.7	30.7	22.8	22.7	3.8	3.9	3.5	3.5	4.0
$Yb_2L_3 \cdot 7H_2O$	35.8	35.8	26.1	26.1	4.3	4.5	2.4	2.4	4.5
$Lu_2L_3 \cdot 20H_2O$	29.0	29.0	20.9	21.0	3.0	3.3	4.1	4.2	4.3

* $L = C_5H_3N(COO^-)_2$.

Table 2
Frequencies of maximum of absorption bands in IR spectra of isocinchomeronic acid and isocinchomeronates of Y, lanthanides and Na (cm^{-1})

Complex	νOH	σOH	νCOOH	$\nu_{as}COO^-$	$\nu_s COO^-$	νCN	νC–H	νMc–O
$C_7H_5NO_4$			1729	1597	1385	1257, 1129	937–557	
$Y_2L_3\cdot 8H_2O$	3448	1176 1160		1610 1580	1420 1375	1290 1110	950–540	460
$La_2L_3\cdot 14H_2O$	3400	1176 1150		1610 1585	1405 1376	1280 1110	960–516	460
$Ce_2L_3\cdot 16H_2O$	3400	1175 1150		1640 1610	1410 1390	1280 1110	960–520	450
$Pr_2L_3\cdot 14H_2O$	3400	1188 1160		1610 1590	1410 1375	1300 1120	960–540	450
$Nd_2L_3\cdot 7H_2O$	3368	1180 1160		1610 1590	1410 1390	1275 1100	960–540	450
$Sm_2L_3\cdot 7H_2O$	3424	1176 1160		1625 1595	1430 1395	1295 1110	950–540	460
$Eu_2L_3\cdot 6H_2O$	3424	1180 1160		1610 1585	1410 1370	1290 1110	950–540	460
$Gd_2L_3\cdot 12H_2O$	3393	1188 1150		1620 1584	1410 1390	1280 1110	950–516	460
$Tb_2L_3\cdot 6H_2O$	3424	1180 1150		1620 1580	1420 1380	1288 1110	950–540	460
$Dy_2L_3\cdot 12H_2O$	3440	1175 1150		1610 1590	1410 1380	1280 1110	950–540	460
$Ho_2L_3\cdot 14H_2O$	3480	1175 1150		1610 1580	1410 1380	1280 1110	950–540	460
$Er_2L_3\cdot 13H_2O$	3464	1180 1155		1620 1580	1410 1370	1290 1110	950–560	460
$Tm_2L_3\cdot 15H_2O$	3470	1175 1150		1620 1580	1420 1380	1280 1110	950–540	460
$Yb_2L_3\cdot 7H_2O$	3448	1180 1155		1610 1590	1410 1390	1280 1110	950–540	460
$Lu_2L_3\cdot 20H_2O$	3384	1185 1155		1610 1584	1400 1390	1288 1120	960–540	455
$Na_2L\cdot xH_2O$	3400	1185 1135		1610	1410	1290 1120	960–550	450

$L^* = C_5H_3N(COO^{\ominus})_2$

maxima at 950–960 cm^{-1} and 516–560 cm^{-1}, and the bands of the metal-oxygen bond appear at 450–460 cm^{-1}. The absorption bands of C–N in the prepared complexes are shifted insignificantly compared to the respective band of isocinchomeronic acid, what indicates that the nitrogen atom at pyridine ring does not take part in the coordination of Ln(III) ions. The metal ions are coordinated only by the oxygen atoms of carboxylate groups and water molecules. The separation values ($\Delta\nu$) of $\bar{\nu}_{as}$(OCO) and $\bar{\nu}_s$(OCO) in the IR spectra of the Y and lanthanide complexes ($\Delta = 198$–$225\ cm^{-1}$) are very similar to this value in the sodium salt ($\Delta = 200\ cm^{-1}$), which indicates a notable participation of the ionic bond in the prepared isocinchomeronates. The bands of asymmetric and symmetric vibrations of OCO^- group are split and they are shifted insignificantly to higher and lower frequencies, what permit to suggest that mode of COO^- group coordination is different and that the COO^- groups act as monodentate and bidentate bridging. The water molecules are in the inner and the outer coordination sphere.

The rare earth hydrated isocinchomeronates are stable up to 328–410 K and then during heating in static air they are decomposed in different ways (Table 3, Figs 1–4). The complexes of Y(III), Nd(III)–Tb(III) and Yb(III) heated lose all water molecules in one step and then the anhydrous ones decompose directly to the oxides Ln_2O_3 and Tb_4O_7 (Figs. 1, 4). Lanthanum (III) complex upon heating decomposes in four steps. This complex heated lose crystallization water molecules in two steps (322 K, 517 K) and the anhydrous complex decomposes to oxide with intermediate formation oxocarbonate (Fig. 2). Lutetium (III) complex heated lose crystallization water molecules in two steps (328 K, 511 K) and next the anhydrous one decomposes directly to Lu_2O_3 (Fig. 4). During heating, the hydrated complexes of Pr(III), Er(III) and Dy(III) lose

Table 3
Data on dehydration and decomposition of Y and lanthanide isocinchomeronates.

Complex	Temp. range of dehydration in K	Mass loss %		Loss of H_2O mol	Temp. range of decomposition in K	Mass loss %		Temp. of oxide formation in K
		Calc.	Found			Calc.	Found	
Y_2L_3*·$8H_2O$	332–603	17.6	17.5	8	674–1063	72.4	72.5	1063
La_2L_3·$14H_2O$	322–484	19.3	19.0	11	713–1147	68.2	70.0	1147
	517–673	5.3	6.0	3				
Ce_2L_3·$16H_2O$	335–461	8.5	8.6	5				
	494–658	13.5	13.2	8	660–987	67.6	67.7	987
Pr_2L_3·$14H_2O$	323–623	20.9	20.4	12	643–923	67.0	67.0	923
Nd_2L_3·$7H_2O$	353–525	13.9	14.2	7	720–1044	63.0	63.0	1044
Tm_2L_3·$7H_2O$	348–573	13.7	14.0	7	696–1064	62.2	62.3	1064
Eu_2L_3·$6H_2O$	328–539	11.9	12.0	6	672–1007	61.2	61.0	1007
Gd_2L_3·$12H_2O$	337–675	21.0	21.0	12	697–1063	64.7	65.0	1063
Tb_2L_3·$6H_2O$	341–550	11.8	12.0	6	702–993	59.3	59.0	993
Dy_2L_3·$12H_2O$	337–686	17.5	17.8	10	693–1025	63.6	63.8	1025
Ho_2L_3·$14H_2O$	333–507	8.4	8.5	5	702–1029	64.9	65.0	1029
	513–654	11.7	11.6	7				
Er_2L_3·$13H_2O$	373–659	18.6	18.7	11	673–1017	64.0	63.8	1017
Tm_2L_3·$15H_2O$	403–502	6.5	6.6	4				
	505–651	14.7	14.9	9	673–1026	65.0	65.1	1026
Yb_2L_3·$7H_2O$	333–623	13.0	13.0	7	723–1028	59.4	59.3	1028
Lu_2L_3·$20H_2O$	328–483	19.4	19.4	13				
	511–691	10.4	10.2	7	693–950	67.0	67.0	950

*L = $C_5H_3N(COO^-)_2$

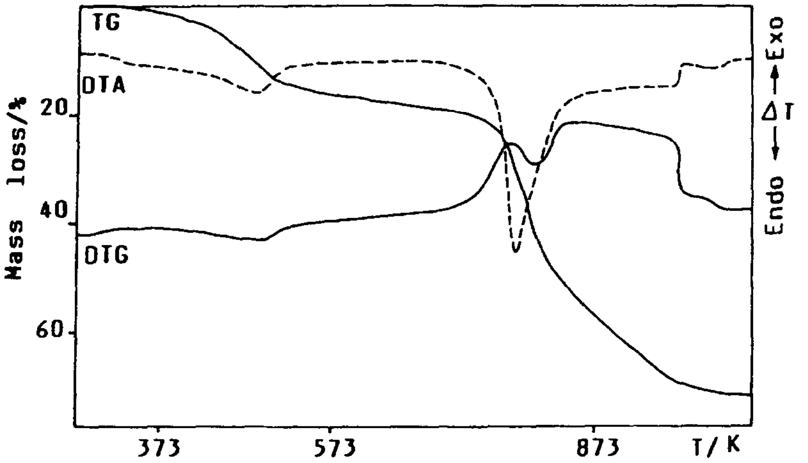

Fig. 1. TG, DTG and DTA curves of $Y_2(C_7H_3NO_4)_3 \cdot 8H_2O$

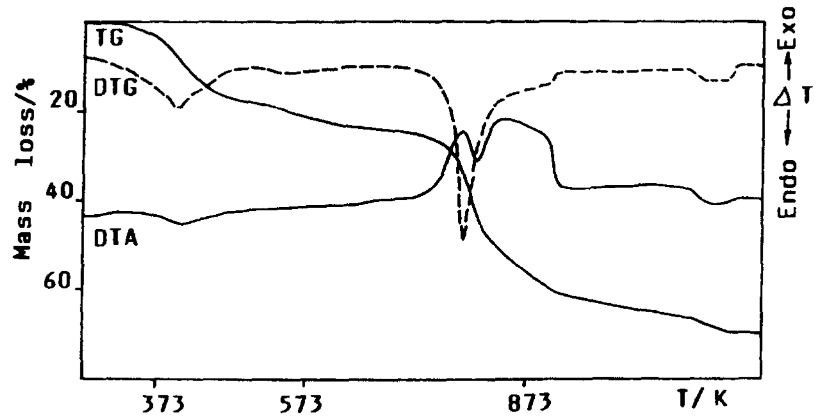

Fig. 2. TG, DTG and DTA curves of $La_2(C_7H_3NO_4)_3 \cdot 14H_2O$

some of their crystallization water molecules in one step and then hydrated complexes decompose directly to the oxides. The hydrated complexes of Ce(III), Ho(III) and Tm(III) (Figs 3) decompose in three steps. They lose some crystallization water molecules in two steps and then hydrated ones are dehydrated and decomposed simultaneously directly to the oxides CeO_2 and Ln_2O_3.

The obtained results indicate that the thermal decomposition of Y and lanthanide isocinchomeronates can be presented in the following manner:

$Ln_2L_3 \cdot xH_2O \rightarrow Ln_2L_3 \rightarrow Ln_2O_3$, Tb_4O_7 Ln = Y, Nd, Sm, Gd, Tb, Yb $x = 6$–12

$La_2L_3 \cdot 14H_2O \rightarrow Ln_2L_3 \cdot 3H_2O \rightarrow La_2L_3 \rightarrow La_2O_2CO_3 \rightarrow La_2O_3$

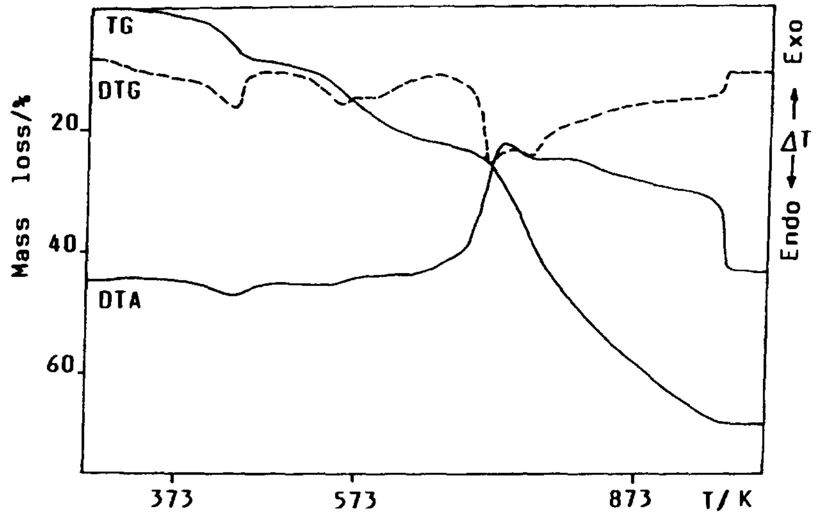

Fig. 3. TG, DTG and DTA curves of $Ce_2(C_7H_3NO_4)_3 \cdot 16H_2O$

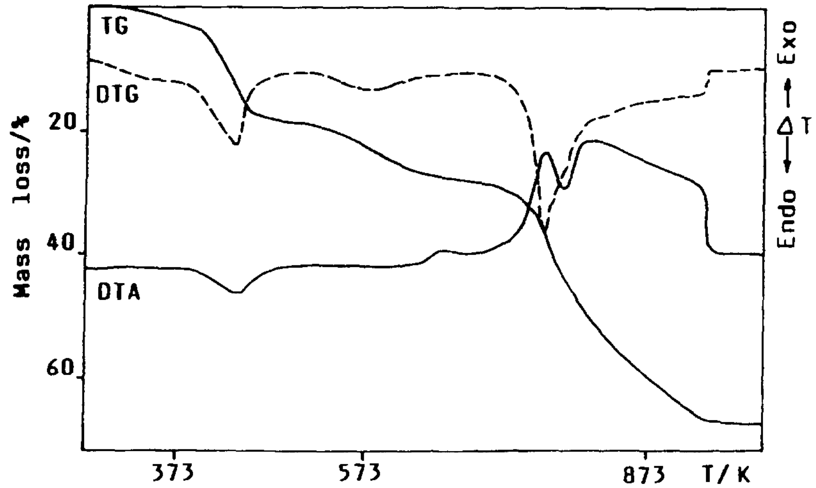

Fig. 4. TG, DTG and DTA curves of $Lu_2(C_7H_3NO_4)_3 \cdot 20H_2O$

$Lu_2L_3 \cdot 20H_2O \rightarrow Lu_2L_3 \cdot 7H_2O \rightarrow Lu_2O_3$

$Ln_2L_3 \cdot xH_2O \rightarrow Ln_2L_3 \cdot 2H_2O \rightarrow Ln_2O_3, Pr_6O_{11}$

$Ln = Pr, Er, Dy$

$Ln_2L_3 \cdot xH_2O \rightarrow Ln_2O_3 \cdot yH_2O \rightarrow Ln_2L_3 \cdot zH_2O \rightarrow Ln_2O_3, CeO_2$

$Ln = Ce, Ho, Tm \quad x > y > z$

In general it can be suggested that hydrated rare earth isocinchomeronates when heated lose all or some water molecules in one or two steps and then decompose to the oxides either directly or with intermediate formation of oxocarbonates.

The dehydration and decomposition of the complexes are connected with a strong endothermic effect, whereas the combustion of the organic ligand and the products of its decomposition – with exothermic ones.

On the basis of the IR spectra and thermal curves it is possible to suggest that the water molecules present in rare earth isocinchomeronates are bonded in different ways: as inner sphere water coordinated to metal ion, outer sphere water connected by hydrogen bond with coordination sphere of the complexes and lattice water (in strongly hydrated complexes).

The temperatures of the dehydration (T_0), the temperatures of decomposition (T) of the complexes and the temperatures of oxide formation (T_k) in the lanthanide series are presented on Fig. 5. The values of the dehydration temperatures of the prepared complexes similarly as of dipicolinates [9] change irregularly with increasing atomic number of metal whereas for rare earth lutidinates [10] they change regularly. The temperatures of decomposition for the anhydrous as well as for hydrated complexes change insignificantly in the lanthanide series (from 643 K for Pr to 723 K for Tm). The temperatures of oxide formation change from 923 K for Ce to 1147 K for La; for heavy lanthanides they change insignificantly.

Isocinchomeronates of Y(III) and lanthanide (III) are sparingly soluble in water (Table 1). Their solubilities are of the order 10^{-5} mol dm^{-3} and change in the lanthanide series (Fig. 6). The solubilities of the prepared complexes decrease from La to Eu and then increase to Dy. The solubilities of the complexes of heavy lanthanides change insignificantly. The Y complex is the most soluble. In this case the Y complex is similar to the complexes of light lanthanides.

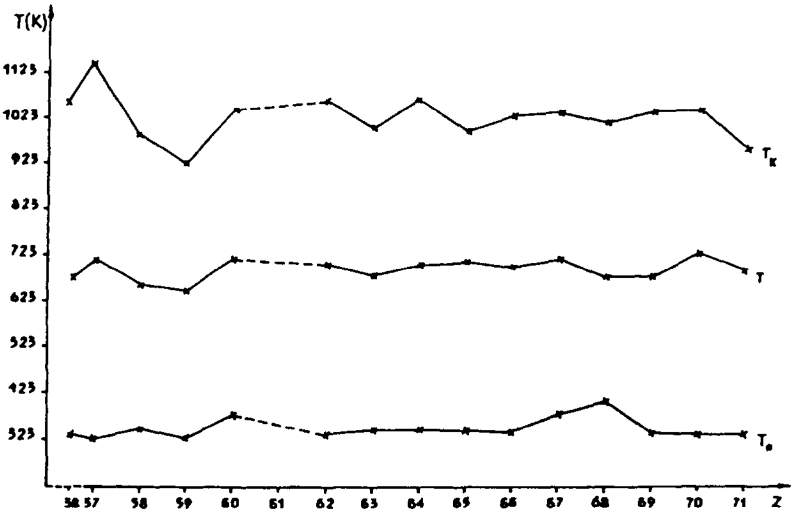

Fig. 5. Relationship between T_0, T, T_k and Z of Ln(III)

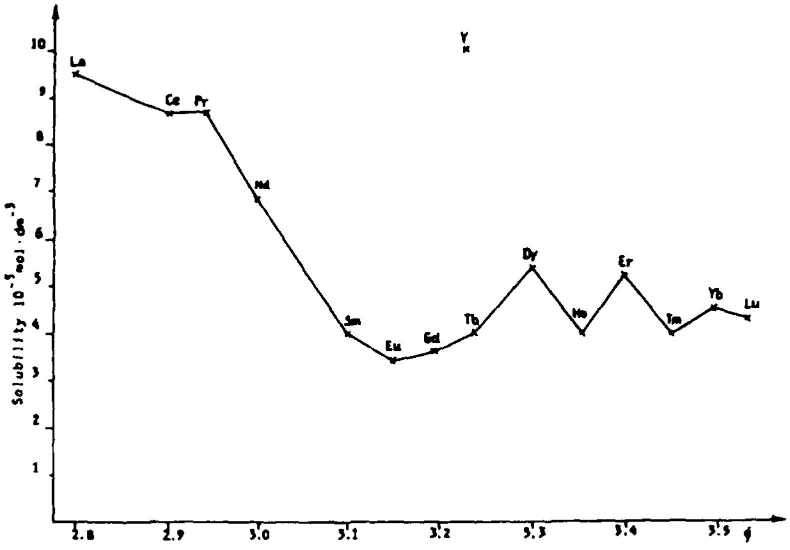

Fig. 6. Relationship between solubility and ionic potential ϕ of Ln(III)

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